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1976

Interpenetrating polymer networks as piezodialysis membranes

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INTERPENETRATING POLYMER NETWORKS

AS PIEZODIALYSIS MEMBRANES

by

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A Research Report

Presented in Partial Fulfillment of

the Requirements for the Degree of

Master of Science

in

Chemical Engineering

Lehigh University

1976

CERTIFICATE OF APPROVAL

This research report is accepted and approved in
partial fulfillment of the requirements for the
degree of Master of Science.

12/23/76
(Date)

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ABSTRACT

Piezodialysis is a new membrane process for water desalination but still far from a practical reality. In this process a concentrated salt solution is forced by high pressure to pass through a special membrane leaving behind fresh water or water with reduced salinity compared to the feed. Ideal membranes for piezodialysis are called charge mosaic membranes. These membranes are composed of discrete, uniform regions of anion and cation exchangers which extend continuously from one surface of the membrane to the other.

Interpenetrating Polymer Network (IPN) membranes were synthesized from styrene and 4-vinyl pyridine. The polystyrene phase (Polymer 1) was converted to cation exchanger and the poly(4-vinyl pyridine) (Polymer 11) was converted to anion exchanger. These (IPN) membranes are not mosaic membranes. Their potential use as piezodialysis membranes was investigated and some of them did show piezodialysis effects. Two of the membranes tested under high pressure gave permeates which were found to be more concentrated in sodium chloride than the initial feed solution, when analyzed by Differential Refractometry. The permeates from the second membrane were double checked by titrating the chloride ion with silver nitrate solution. The results of the titration also indicated positive effect.

INTRODUCTION

When a solution is separated from pure solvent by a
semipermeable membrane which allows the passage of solvent
molecules but not those of the solute, there is a tendency
to equalize the concentrations on both sides of the membrane.
The solvent molecules diffuse through the membrane and pass to
the solution side until concentrations are equal on both sides
of the membrane. This is known as Osmosis and the increase in
pressure on the solution side caused by the incoming solvent
molecules is called Osmotic Pressure. If a pressure is applied
on the solution side, the flow of solvent molecules will slow
down and stop completely when the applied pressure is equal to
the Osmotic Pressure of the solution. When the applied pressure
is greater than the Osmotic Pressure the flow of solvent will be
from the solution to the solvent side. This phenomenon is
called Reverse Osmosis and is applied in the desalination of
brackish waters. The membranes employed in Reverse Osmosis
desalination are mostly made of cellulose acetate, which are
in flat sheet or tubular form. These membranes are usually
plain ones with no ionic charges but charged Reverse Osmosis
membranes can also be used.[1] Another membrane material used
in commercial Reverse Osmosis units is an aromatic polyamide
hydrazide.

In piezodialysis the membrane is more permeable to
solute than to solvent. Instead of water or solvent a con-
centrated salt solution passes through the membrane under the

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effect of the high pressure applied leaving behind water with reduced salinity. The advantage of piezodialysis is that mainly salt, the minor component of the solution passes through the membrane while in ordinary reverse osmosis water, the major component is transported through the membrane.

Although no commercial desalination units based on piezodialysis have been realized yet, the mathematical theory of piezodialysis seems to be well established. Kedem and Katchalsky[2] have derived detailed equations describing fluxes and transport coefficients through a composite membrane. Similarly Leitz and Sharr[3] have modified slightly the Kedem and Katchalsky treatment and derived theoretical equations which can be used with assumed variables to predict membrane performance. More theoretical treatmemts can be found in literature[4-9] and will not be discussed here.

What makes piezodialysis still far from being a practical desalination process is the difficulty encountered in making the essential charge mosaic membrane. Platt and Schindler[10] list the principal features of a charge mosaic membrane of high efficiency in piezodialysis as follows:

1. Each ionic domain should pass uninterrupted through the membrane.
2. The ionic concentration in both anionic and cationic domains should be similar and as high as possible.
3. Both kinds of domains should be of equal size.
4. The membrane should possess sufficient mechanical strength to sustain the applied pressure.

This list can be extended easily. For example, having a high coupling ratio, being as thin as possible and chemical

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stability and inertness are other important properties
desired in a piezodialysis membrane. Efforts to make a
charge mosaic membrane have started only a decade ago.
Since 1965 several groups of investigators were involved
in the preparation of charge mosaic membranes. So far only
two charge mosaic membranes were made which had most of the
desired properties, but not all. The first charge mosaic
membrane was prepared by embedding manually alternating
cation and anion exchange beads in an impermeable silicone
rubber matrix.[11] This was a very small membrane of about
0.06 cm^2 in area. The investigators have used it to study
coupled flow processes and measure some coefficients and no
high pressure piezodialysis runs were carried out with this
membrane. The other membrane was prepared by Leitz and
Sharr[3] who call their method thermal lamination. Here,
styrenized polyethylene membranes in the anion and cation
form were used. A large number of alternating cation and
anion exchange membranes were stacked and thermally laminated
into a block. Then thin slices were cut perpendicular to the
resin surfaces. This way membranes were obtained composed of
alternating stripes of cation and anion exchange resins.
Apparently both of these methods gave very small membranes
and they cannot be applied to large scale membrane production.
The need for a different or new method of actually synthesiz-
ing efficient charge mosaic membranes is still very alive.

Ionic Interpenetrating Polymer Networks (IPN) was thought to be one possibility. An IPN is synthesized by swelling a cross-linked polymer (I) with a second monomer (II) containing its own crosslinker and initiator, and polymerizing monomer II in situ.[12] In this work no attempts were made to produce mosaic membranes but the potential use of cationic-anionic IPN's as piezodialysis membranes was investigated.

EXPERIMENTAL

Synthesis:

The synthesis of anionic/cationic IPN membranes was carried out in four basic steps. Styrene was first polymerized using an U-V light source, between glass plates separated by a thin Teflon gasket to form the initial material. Most of the membranes were made from styrene containing 1% divinyl benzene as cross-linker and 0.3% benzoin as initiator. The cross-linker was later reduced to 0.5% and 0.25%.

The polystyrene film was then swollen with 4-vinyl pyridine containing the same cross-linking agent and initiator as before. 2-3% divinyl benzene was used with monomer II. 4-vinyl pyridine was then polymerized, thus the interpenetrating polymer network (IPN) was obtained with polystyrene as polymer I and poly (4-vinyl-pyridine) as polymer II.

The third step involved the introduction of the positive fixed charge groups to polymer II. The IPN was immersed in a solution of n-butyl bromide and nitromethane to quaternize the pyridine rings. The quaternization was carried out at a temperature of 45°C and lasted for 24 hours.

Finally the membrane was subjected to sulphonation. It was placed in concentrated sulphuric acid containing 0.1% Ag_2SO_4 as catalyst and let react for 1-2 hours at 40-45°C. The membranes were conditioned in salt water of the same composition as the feed solution to be used before testing.

Results:

The elemental analysis, together with the IPN composition and extent of sulphonation and quaternization of some of these membranes are shown in Table 1. The elemental analysis was done in Robertson Laboratory, Florham Park, New Jersey; and the IPN composition was calculated on the basis of Nitrogen content. The membranes were tested for piezodialysis in a high pressure cell, Model M420, supplied by Amicon Corp., Lexington, Mass. This cell calls for a 7.62 cm diameter membrane but because the membranes were rather brittle and often cracked during the synthesis it was extremely difficult to employ a 7.62 cm membrane. Secondary discs were used with small holes in the center to test smaller size membranes. The cell was pressurized by N_2 and the feed solution (0.1% NaCl) was constantly stirred by a magnetic stirrer installed in the pressure cell.

The permeates were collected in small preweighed containers. They were analyzed for NaCl by Differential Refractometer. (Brice-Phoenix Differential Refractometer. Visual Laboratory Type, Model BP-2000-V). The Δn values were converted to concentrations by weight of NaCl. The pressure applied was 1.03×10^7 N/m^2.

Membrane M21 showed positive piezodialysis effects. However, the salt enrichment dropped with time. The performance of M21 is shown in Fig. 1. A small piece of M21

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Table 1: Elemental Analysis*and IPN Composition showing extent of sulphonation and quaternization

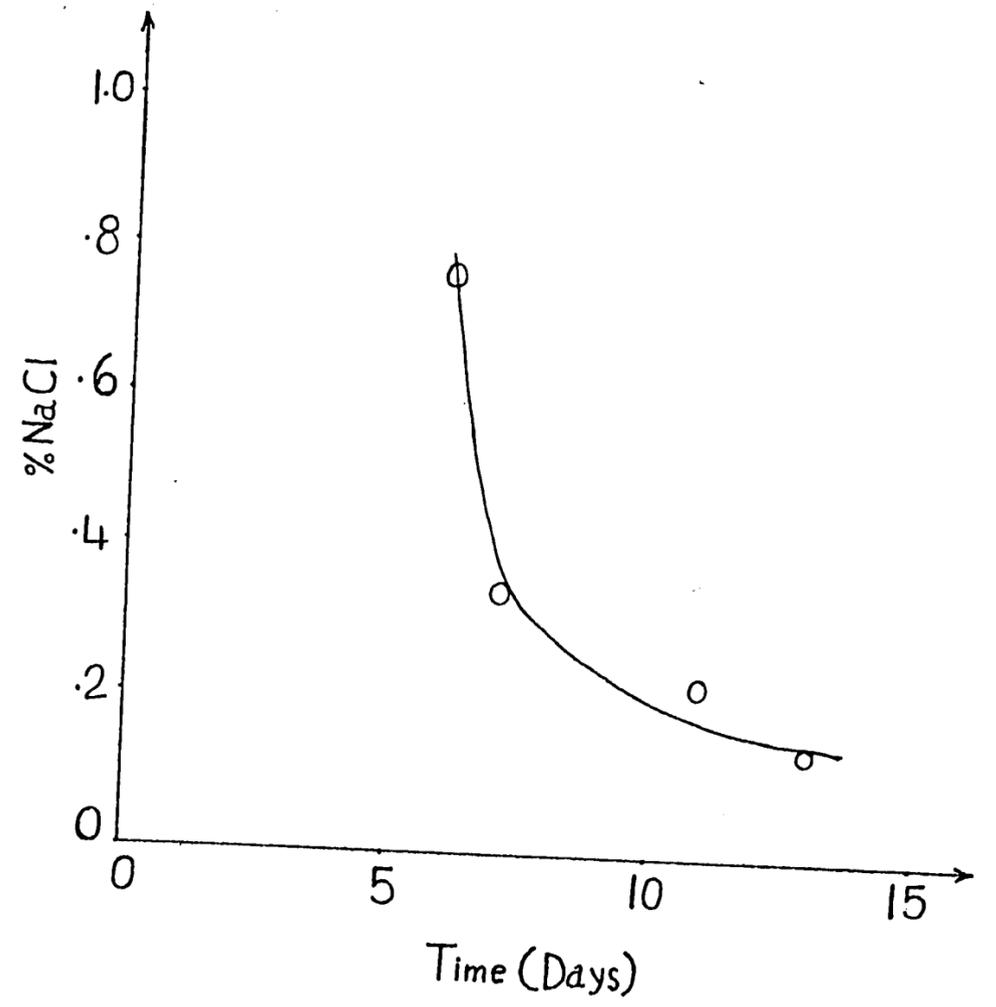| Mem.	C	H	N	S	Cl	P.I	% DVB	P.II	% DVB	%Sul.	%Qua.
M9	59.08	6.16	1.77	6.11	3.37	78.4	1	21.6	0.5	41.7	75.1
M10	57.78	4.47	4.42	4.29	6.85	41.8	1	58.2	0.5	59.1	61.1
M21	59.30	7.76	4.94	2.00	12.69	27.1	1	72.9	2	47.2	100
M22	54.93	7.24	4.78	3.97	7.25	33.2	1	66.8	2	72.5	59.8
M23	52.97	7.13	4.77	4.85	4.86	35.9	1	64.1	2	78.8	40.2
M24	53.33	7.30	4.43	4.20	5.20	39.1	.5	60.9	3	63.9	46.3

*Balance is Sodium + Oxygen

Fig. 1 Salt concentration vs time for permeates from M21

was analyzed after the test run. It was found that the membrane was very stable chemically and almost the same analysis was reported as before testing.

Another membrane which showed piezodialysis effects is M24. The analysis of permeates from this membrane is shown in Table 2. Four permeates were collected and these were analyzed both by Differential Refractometer and by titration with $AgNO_3$. The difference between the two results can be attributed to the iron contamination in the permeates. The presence of iron was detected by spectrophotometry. Upon detection of iron in the permeates four solutions were prepared containing 0.1% NaCl plus $FeCl_3$ in amounts corresponding to the iron present in each permeate. These solutions were then analyzed by Differential Refractometer. Table 3 shows the results of this analysis. The % NaCl determined was less than the initial values obtained by D.R. for the permeates, showing that the high values were not due to iron present in the permeates. The initial and corrected values of % NaCl by D.R. are listed in Table 4. When M24 was tested with a little more concentrated feed (0.3% NaCl) salt depletion was observed in the permeates rather than salt enrichment.

In Table 5, the mass flux, and permeability coefficients of M24 are compared with those of the first charge mosaic and cellulose acetate reverse osmosis membranes.

Table 2: Analysis of Permeates from Membrane M24

Solution	%NaCl by D.R.	Nor. N by Titra.	%NaCl by Titra.	Iron ppm
Feed Stock	0.100	0.0176	0.1029	1.00
Permeate 1	0.153	0.0184	0.1075	56.2
Permeate 2	0.265	0.0367	0.2148	82.2
Permeate 3	0.280	0.0394	0.2307	79.6
Permeate 4	0.300	0.0357	0.2090	76.8

Table 3: Analysis of Feed Stock + $FeCl_3$

Solution	% NaCl by D.R.	D.R. error
Feed Stock 0.1% NaCl	0.108	
Feed + 56.2 ppm Fe.	0.115	0.007
Feed + 82.2 ppm Fe.	0.127	0.019
Feed + 79.6 ppm Fe.	0.125	0.017
Feed + 76.8 ppm Fe.	0.121	0.013

Table 4: Initial and Corrected Values of % NaCl in Permeates from M24

Solution	% NaCl by D.R.	Iron ppm	Corrected % NaCl by D.R.
Permeate 1	0.153	56.2	0.146
Permeate 2	0.265	82.2	0.246
Permeate 3	0.280	79.6	0.263
Permeate 4	0.300	76.8	0.287

Table 5:   Mass Flux and Permeability Coefficients

Membrane	J gm/cm^2. sec.	$gm\ cm/cm^2$.atm. sec.
Mosaic M4[a]	1.49×10^{-6}	1.06×10^{-7}
Coxe Lab. M24	1.95×10^{-6}	2.43×10^{-10}
R.O. Cellulose Acetate[b]	1×10^{-3}	5.1×10^{-8}

a: Based on data from reference 11

b: From reference 1

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